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(54) **Improved processability of silica filled rubber stocks**

(57) A processable rubber stock is produced by the preparation of a silica-filled, elastomeric compound comprising mixing an elastomer with an amorphous silica filler, from 0 to less than about 1 % by weight based on said silica filler of bis[3-(triethoxysilyl)propyl]tetrasulfide, an alkylalkoxysilane and a cure agent. A further processing aid comprising at least one of an ester of a fatty acid or an ester of a polyol is preferred. The elastomer is preferably a diene monomer homopolymer or a copolymer of at least one diene and at least one monovinyl aromatic monomer. By effecting vulcanization, a vulcanized elastomeric compound is produced containing good physical properties for use as tread for a pneumatic tire.

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## Description

## TECHNICAL FIELD

5 The subject invention relates to the processing and vulcanization of diene polymer and copolymer elastomer containing rubber stocks. More specifically, the present invention relates to the processing and vulcanization of diene polymer and copolymer elastomer-containing, silica-filled rubber stocks using a mixture of silanes as processing aids.

## BACKGROUND OF THE INVENTION

10 In the art it is desirable to produce elastomeric compounds exhibiting reduced hysteresis when properly compounded with other ingredients such as reinforcing agents, followed by vulcanization. Such elastomers, when compounded, fabricated and vulcanized into components for constructing articles such as tires, power belts, and the like, will manifest properties of increased rebound, decreased rolling resistance and less heat-build up when subjected to  
15 mechanical stress during normal use.

The hysteresis of an elastomer refers to the difference between the energy applied to deform an article made from the elastomer and the energy released as the elastomer returns to its initial, undeformed state. In pneumatic tires, lowered hysteresis properties are associated with reduced rolling resistance and heat build-up during operation of the tire. These properties, in turn, result in lowered fuel consumption of vehicles using such tires.

20 In such contexts, the property of lowered hysteresis of compounded, vulcanizable elastomer compositions is particularly significant. Examples of such compounded elastomer systems are known to the art and are comprised of at least one elastomer (that is, a natural or synthetic polymer exhibiting elastomeric properties, such as a rubber), a reinforcing filler agent (such as finely divided carbon black, thermal black, or mineral fillers such as clay and the like) and a vulcanizing system such as sulfur-containing vulcanizing (that is, curing) system.

25 Previous attempts at preparing readily processable, vulcanizable, silica-filled rubber stocks containing natural rubber or diene polymer and copolymer elastomers have focused upon the sequence of adding ingredients during mixing (Bomal, et al., *Influence of Mixing procedures on the Properties of a Silica Reinforced Agricultural Tire Tread*, May 1992), the addition of de-agglomeration agents such as zinc methacrylate and zinc octoate, or SBR-silica coupling agents such as mercapto propyl trimethoxy silane (Hewitt, *Processing Technology of Silica Reinforced SBR, Elastomerics*, pp 33-37, March 1981), and the use of bis[3-(triethoxysilyl)propyl]tetrasulfide (Si69) processing aid (Degussa, PPG).

The use of Si69 processing aid in the formulation of silica-filled rubber stocks has been successful, but generally requires a large amount of the additive, such as 10 % by weight based on the weight of silica, in order to be effective.

35 Precipitated silica has been increasingly used as a reinforcing particulate filler in carbon black-filled rubber components of tires and mechanical goods. Silica-loaded rubber stocks, however, exhibit relatively poor processability.

The present invention provides a mixture of silanes for use as processing aids for silica-filled rubber stocks, which greatly improve the processability and properties of the formulations and resulting vulcanized product.

## SUMMARY OF INVENTION

40 It is therefore an object of the present invention to provide rubber stock processing aids which improve the processability of formulations of diene polymer elastomers with silica-filler.

It is another object of the present invention to provide a method for reducing the viscosity of silica-filled elastomeric vulcanizable compounds.

45 It is another object of the present invention to provide a method for enhancing the processability of silica-filled elastomeric vulcanizable compounds.

It is another object of the present invention to provide vulcanizable silica-filled elastomeric compounds having enhanced physical properties.

50 The foregoing objects, together with the advantages thereof over the existing art, which shall become apparent from the specification which follows, are accomplished by the invention as hereinafter described and claimed.

The present invention provides a process for the preparation of a silica-filled, vulcanized elastomeric compound comprising: mixing an elastomer with an amorphous silica filler, from 0 to less than about 1 % by weight based on said silica filler of bis[3-(triethoxysilyl)propyl]tetrasulfide, an alkylalkoxysilane and a cure agent; and, effecting vulcanization. Preferably, the elastomer is a diene monomer homopolymer or a copolymer of a diene monomer and a monovinyl aromatic monomer.

55 The present invention further provides a vulcanizable silica-filled compound comprising an elastomer, a silica filler, from 0 to less than about 1 % by weight based on said silica filler of bis[3-(triethoxysilyl)propyl]tetrasulfide (Si69), an alkylalkoxysilane and a cure agent. Preferably, the elastomer is styrene butadiene rubber, optionally containing a car-

bon black filler. The compound is more readily processable during mixing, due to the use of the mixture of silane processing aids.

The present invention further provides a pneumatic tire comprising tread stock vulcanized from the inventive vulcanizable silica-filled compound.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In general, the present invention provides a means to reduce the level of Si69 needed to obtain good physical properties in a cured rubber stock containing silica as a filler. In addition, the present invention further provides maintenance of the processability of the compounded stock, as measured by Mooney viscosity, at the same level as achieved with high levels of Si69.

The present invention utilizes the presence of an alkylalkoxysilane as a silica hydrophobating agent, such that minimal amounts of Si69 are needed to obtain good processability, and yet still give good physical properties. According to the invention, therefore, a less costly silane can be substituted for the majority or all of the Si69 that would be normally used without any loss of processability or properties. Additionally, remilling can be eliminated, and the cure of the rubber stock is not dependent on the high sulfur level present in the Si69.

The silica-hydrophobating agents useful according to the present invention include those alkylalkoxysilanes of the formula  $(R_1)_2Si(OR_2)_2$  or  $R_1Si(OR_2)_3$ , wherein the alkoxy groups are the same or are different; each  $R_1$  independently comprising C1 to about C18 aliphatic, about C6 to about C12 cyclo-aliphatic, or about C6 to about C18 aromatic, preferably C1 to about C10 aliphatic, about C6 to about C10 cyclo-aliphatic, or about C6 to about C12 aromatic; and each  $R_2$  independently containing from one to about 6 carbon atoms. Representative examples include octyltriethoxy silane, octyltrimethoxy silane, (3-glycidoxypentyl)triethoxy silane, (3-glycidoxypentyl)triethoxy silane, hexyltriethoxy silane, ethyltriethoxy silane, propyltriethoxy silane, phenyltriethoxy silane, cyclohexyltriethoxy silane, cyclohexyltriethoxy silane, dimethyldimethoxy silane, 3-chloropropyltriethoxy silane, methacryloxytriethoxy silane, i-butyltriethoxy silane, and the like. Of these, octyltriethoxysilane is preferred.

According to the present invention, polymerized elastomer is compounded in the rubber stock, e.g., polybutadiene, polyisoprene and the like, and copolymers thereof with monovinyl aromatics such as styrene, alpha methyl styrene and the like, or trienes such as myrcene. Thus, the elastomers include diene homopolymers, A, and copolymers thereof with monovinyl aromatic polymers, B. Exemplary diene homopolymers are those prepared from diolefin monomers having from 4 to about 12 carbon atoms. Exemplary vinyl aromatic polymers are those prepared from monomers having from 8 to about 20 carbon atoms. Examples of conjugated diene monomers and the like useful in the present invention include 1,3-butadiene, isoprene, 1,3-pentadiene, 2,3-dimethyl-1,3-butadiene and 1,3-hexadiene, and aromatic vinyl monomers include styrene,  $\alpha$ -methylstyrene, p-methylstyrene, vinyltoluenes and vinylnaphthalenes. The conjugated diene monomer and aromatic vinyl monomer are normally used at the weight ratios of about 90:10 to about 55:45, preferably about 80:20 to about 65:35.

Preferred elastomers include diene homopolymers such as polybutadiene and polyisoprene and copolymers such as styrene butadiene rubber (SBR). Copolymers can comprise from about 99 to 20 percent by weight of diene units and from about 1 to about 80 percent by weight of monovinyl aromatic or triene units, totaling 100 percent. The polymers and copolymers of the present invention may have the diene portion with a 1,2-microstructure contents ranging from about 10 to about 80 percent, with the preferred polymers or copolymers having 1,2-microstructure contents of from about 25 to 65 percent. The molecular weight of the polymer that is produced according to the present invention, is preferably such that a proton-quenched sample will exhibit a gum Mooney viscosity ( $ML_4/212^\circ F$ ) of from about 2 to about 150. The copolymers are preferably random copolymers which result from simultaneous copolymerization of the monomers, as is known in the art. Also included are nonfunctionalized cispolybutadiene, ethylene-propylene-diene monomer (EPDM), emulsion SBR and natural rubber.

Initiators known in the art such as an organolithium initiator, preferably an alkylolithium initiator, can be employed to prepare the elastomer. More particularly, the initiators used in the present invention include N-lithio-hexamethyleneimine, organolithium compounds such as n-butyllithium, tributyltin lithium, dialkylaminolithium compounds such as dimethylaminolithium, diethylaminolithium, dipropylaminolithium, dibutylaminolithium and the like, dialkylaminoalkylolithium compounds such as diethylaminopropylolithium and the like, and trialkyl stanyl lithium, wherein the alkyl group contains 1 to about 12 carbon atoms, preferably 1 to about 4 carbon atoms.

Polymerization is usually conducted in a conventional solvent for anionic polymerizations such as the various cyclic and acyclic hexanes, heptanes, octanes, pentanes, their alkylated derivatives, and mixtures thereof. Other techniques for polymerization, such as semi-batch and continuous polymerization may be employed. In order to promote randomization in copolymerization and to increase vinyl content, a coordinator may optionally be added to the polymerization ingredients. Amounts range between 0 to 90 or more equivalents per equivalent of lithium. The amount depends upon the amount of vinyl desired, the level of styrene employed and the temperature of the polymerizations, as well as the nature of the specific polar coordinator employed.

Compounds useful as coordinators are organic and include those having an oxygen or nitrogen hetero-atom and a non-bonded pair of electrons. Examples include dialkyl ethers of mono and oligo alkylene glycols; "crown" ethers; tertiary amines such as tetramethylethylenediamine (TMEDA); THF; THF oligomers; linear and cyclic oligomeric oxolanyl alkanes, such as 2-2'-di(tetrahydrofuryl) propane, di-piperidyl ethane, hexamethylphosphoramide, N,N'-dimethylpiperazine, diazabicyclooctane, diethyl ether, tributylamine and the like. Details of linear and cyclic oligomeric oxolanyl coordinators can be found in U.S. Pat. No. 4,429,091, owned by the Assignee of record, the subject matter of which is incorporated herein by reference.

Polymerization is usually begun by charging a blend of the monomer(s) and solvent to a suitable reaction vessel, followed by the addition of the coordinator and the initiator solution previously described. Alternatively, the monomer and coordinator can be added to the initiator. The procedure is carried out under anhydrous, anaerobic conditions. The reactants are heated to a temperature of from about 10° to 150°C and are agitated for about 0.1 to 24 hours. After polymerization is complete, the product is removed from the heat and terminated in one or more ways.

To terminate the polymerization, a terminating agent, coupling agent or linking agent may be employed, all of these agents being collectively referred to herein as "terminating agents". Certain of these agents may provide the resulting polymer with a multifunctionality. That is, the polymers initiated according to the present invention, carry at least one amine functional group as discussed hereinabove, and may also carry a second functional group selected and derived from the group consisting of terminating agents, coupling agents and linking agents.

Examples of terminating agents according to the present invention include those commonly employed in the art, including hydrogen, water, steam, an alcohol such as isopropanol, 1,3-dimethyl-2-imidazolidinone (DMI), carbodiimides, N-methylpyrrolidine, cyclic amides, cyclic ureas, isocyanates, Schiff bases, 4,4'-bis(diethylamino) benzophenone, and the like. Other useful terminating agents may include those of the structural formula  $(R_1)_a ZX_b$ , wherein Z is tin or silicon. It is preferred that Z is tin.  $R_1$  is an alkyl having from about 1 to about 20 carbon atoms; a cycloalkyl having from about 3 to about 20 carbon atoms; an aryl having from about 6 to about 20 carbon atoms; or, an aralkyl having from about 7 to about 20 carbon atoms. For example,  $R_1$  may include methyl, ethyl, n-butyl, neophyl, phenyl, cyclohexyl or the like. X is a halogen, such as chlorine or bromine, or an alkoxy ( $-OR_1$ ), "a" is from 0 to 3, and "b" is from about 1 to 4; where  $a + b = 4$ . Examples of such terminating agents include tin tetrachloride,  $(R_1)_3SnCl$ ,  $(R_1)_2SnCl_2$ ,  $R_1SnCl_3$ , and  $R_1SiCl_3$  as well as methyltriphenoxysilane ( $MeSi(OPh_3)$ ).

The terminating agent is added to the reaction vessel, and the vessel is agitated for about 1 to about 1000 minutes. As a result, an elastomer is produced having an even greater affinity for silica compounding materials, and hence, even further reduced hysteresis. Additional examples of terminating agents include those found in U.S. Patent No. 4,616,069 which is herein incorporated by reference. It is to be understood that practice of the present invention is not limited solely to these terminators inasmuch as other compounds that are reactive with the polymer bound lithium moiety can be selected to provide a desired functional group.

Quenching is usually conducted by stirring the polymer and quenching agent for about 0.05 to about 2 hours at temperatures of from about 30° to 120° C to ensure complete reaction. Polymers terminated with a functional group as discussed hereinabove, can be subsequently quenched with alcohol or other quenching agents as described hereinabove.

Lastly, the solvent is removed from the polymer by conventional techniques such as drum drying, extruder drying, vacuum drying or the like, which may be combined with coagulation with water, alcohol or steam, thermal desolventization, or any other suitable method. If coagulation with water or steam is used, oven drying may be desirable.

The elastomeric polymers can be utilized as 100 parts of the rubber in the treadstock compound or, they can be blended with any conventionally employed treadstock rubber which includes natural rubber, synthetic rubber and blends thereof. Such rubbers are well known to those skilled in the art and include synthetic polyisoprene rubber, styrene/butadiene rubber (SBR), polybutadiene, butyl rubber, Neoprene, ethylene/propylene rubber, ethylene/propylene/diene rubber (EPDM), acrylonitrile/butadiene rubber (NBR), silicone rubber, the fluoroelastomers, ethylene acrylic rubber, ethylene vinyl acetate copolymer (EVA), epichlorohydrin rubbers, chlorinated polyethylene rubbers, chlorosulfonated polyethylene rubbers, hydrogenated nitrile rubber, tetrafluoroethylene/propylene rubber and the like. When the polymers discussed hereinabove are blended with conventional rubbers, the amounts can vary widely with a range comprising about 5 to about 99 percent by weight of the total rubber. It is to be appreciated that the minimum amount will depend primarily upon the degree of reduced hysteresis that is desired.

According to the present invention, amorphous silica (silicon dioxide) is utilized as a filler for the diene polymer or copolymer elastomer-containing vulcanizable compound. Silicas are generally classed as wet-process, hydrated silicas because they are produced by a chemical reaction in water, from which they are precipitated as ultrafine, spherical particles.

These primary particles strongly associate into aggregates, which in turn combine less strongly into agglomerates. The surface area, as measured by the BET method gives the best measure of the reinforcing character of different silicas. For silicas of interest for the present invention, the surface area should be about 32 to about 400 m<sup>2</sup>/g, with the range of about 100 to about 250 m<sup>2</sup>/g being preferred, and the range of about 150 to about 220 m<sup>2</sup>/g being most pre-

ferred. The pH of the silica filler is generally about 5.5 to about 7 or slightly over, preferably about 5.5 to about 6.8.

Silica can be employed in the amount of about 1 part to about 100 parts per 100 parts of polymer (phr), preferably in an amount from about 5 to about 80 phr. The useful upper range is limited by the high viscosity imparted by fillers of this type. Some of the commercially available silicas which may be used include: Hi-Sil 215, Hi-Sil® 233, and Hi-Sil 190, all produced by PPG Industries. Also, a number of useful commercial grades of different silicas are available from De Gussa Corporation, Rhone Poulenc, and J.M. Huber Corporation.

The polymers can be compounded with all forms of carbon black in amounts ranging from about 2 to about 50 parts by weight, per 100 parts of rubber (phr), with about 5 to about 40 phr being preferred. The carbon blacks may include any of the commonly available, commercially-produced carbon blacks but those having a surface area (EMSA) of at least 20 m<sup>2</sup>/gram and more preferably at least 35 m<sup>2</sup>/gram up to 200 m<sup>2</sup>/gram or higher are preferred. Surface area values used in this application are those determined by ASTM test D-1765 using the cetyltrimethyl-ammonium bromide (CTAB) technique. Among the useful carbon blacks are furnace black, channel blacks and lamp blacks. More specifically, examples of the carbon blacks include super abrasion furnace (SAF) blacks, high abrasion furnace (HAF) blacks, fast extrusion furnace (FEF) blacks, fine furnace (FF) blacks, intermediate super abrasion furnace (ISAF) blacks, semi-reinforcing furnace (SRF) blacks, medium processing channel blacks, hard processing channel blacks and conducting channel blacks. Other carbon blacks which may be utilized include acetylene blacks. Mixtures of two or more of the above blacks can be used in preparing the carbon black products of the invention. Typical values for surface areas of usable carbon blacks are summarized in the Table I hereinbelow.

TABLE I

Carbon Blacks	
ASTM Designation (D-1765-82a)	Surface Area (m <sup>2</sup> /g) (D-3765)
N-110	126
N-220	111
N-339	95
N-330	83
N-351	74
N-550	42
N-660	35

The carbon blacks utilized in the preparation of the rubber compounds of the invention may be in pelletized form or an unpelletized flocculent mass. Preferably, for more uniform mixing, unpelletized carbon black is preferred.

The reinforced rubber compounds can be cured in a conventional manner with known vulcanizing agents at about 0.2 to about 5 phr. For example, sulfur or peroxide-based curing systems may be employed. For a general disclosure of suitable vulcanizing agents one can refer to Kirk-Othmer, *Encyclopedia of Chemical Technology*, 3rd ed., Wiley Interscience, N.Y. 1982, Vol. 20, pp. 365-468, particularly "Vulcanization Agents and Auxiliary Materials" pp. 390-402. Vulcanizing agents can be used alone or in combination.

Vulcanizable elastomeric compositions of the invention can be prepared by compounding or mixing the elastomeric polymer with silica, optionally carbon black, the silica-hydrophobating agent according to the present invention, a minimal amount of Si69, and other conventional rubber additives including for example, fillers, plasticizers, antioxidants, curing agents and the like, using standard rubber mixing equipment and procedures.

## GENERAL EXPERIMENTAL

In order to demonstrate the preparation and properties of silica-filled, diene elastomer containing rubber stocks prepared according to the present invention, styrene butadiene rubber (SBR) polymers were prepared and were compounded using the formulations set forth in Tables II and III below.

Test results for the Control, C-A, using the Si69 processing aid only, and Examples 1 - 3, using silane processing aids according to the invention in Formulation A, are reported in Table II.

TABLE II

Formulation A for the Partial Replacement of Si69 and Physical Test Results				
Material	Amount (phr)			
Example No.	C-A	1	2	3
SBR	100	100	100	100
Oil	20	20	20	20
Silica	60	60	60	60
Carbon Black	6	6	6	6
Stearic Acid	2	2	2	2
Wax	0.75	0.75	0.75	0.75
Si-69	5.4	0.6	0.6	0.6
Silane (Type)	--	Octyl Trimethoxy	Methacroyl Trimethoxy	Dimethyl Dimethoxy
Silane (Amount)	0	4.71	4.99	3.62
Tackifier	3.5	3.5	3.5	3.5
Antioxidant	0.95	0.95	0.95	0.95
Sulfur	1.4	1.4	1.4	1.4
Accelerators	2.4	2.4	2.4	2.4
Zinc Oxide	3	3	3	3
Physical Properties				
ML <sub>1+4</sub> @ 100°C	93.7	84.7	93.3	88.8
Tensile (psi) @ 23°C	2913	2216	2476	2834
Tensile (psi) @ 100°C	1239	954	1122	1294
% Elong. at break, 23°C	444	603	504	551
% Elong. at break, 100°C	262	407	342	365
Ring Tear (lb/in) @ 100°C	191	198	179	223
Dispersion Index, %	72.9	76.1	84	84.3

Test results for the Control, C-B, using the Si69 processing aid only, and Examples 4 - 7, using silane processing aids according to the invention in Formulation B, are reported in Table III.

TABLE III

Formulation B for the Partial Replacement of Si69 and Physical Test Results					
Material	Amount (phr)				
Example No.	C-B	4	5	6	7
SBR	75	75	75	75	75
BR	25	25	25	25	25
Oil	41.25	41.25	41.25	41.25	41.25
Silica	80	80	80	80	80
Carbon Black	8	8	8	8	8
Stearic Acid	1	1	1	1	1
Wax	1.5	1.5	1.5	1.5	1.5
Si-69	7.2	0.8	0.8	0.8	0.8
Silane (Type)	--	Propyl Triethoxy	3-Chloropropyl Triethoxy	Octyl Triethoxy	i-Butyl Triethoxy
Silane (Amount)	0	5.5	6.42	7.39	5.88
Tackifier	3	3	3	3	3
Antioxidant	1.17	1.17	1.17	1.17	1.17
Sulfur	2.8	2.8	2.8	2.8	2.8
Accelerators	2.4	2.4	2.4	2.4	2.4
Zinc Oxide	1.7	1.7	1.7	1.7	1.7
Physical Properties					
ML <sub>1+4</sub> @ 100°C	64.8	69.2	96.1	53.8	93.9
Tensile (psi) @ 23°C	2497	2268	2566	2400	2513
Tensile (psi) @ 100°C	1453	1278	1693	1280	1379
% Elong. at break, 23°C	487	614	544	612	649
% Elong. at break, 100°C	386	486	487	467	499
Ring Tear (lb/in) @ 100°C	190	270	245	262	298
Dispersion Index, %	93.1	80.5	95.7	87.9	93.3

A series of tests were conducted, in which the Si69 processing aid was omitted and insoluble sulfur was added, while processing Formulation B with 2 phr octyl-triethoxy silane, and 4 phr sorbitan oleate. Test conditions and results are reported for Examples 8-17 and the Control (no added insoluble sulfur), C-C, in Table IV, below.

**TABLE IV**  
Physical Properties of Formulation B with 2 phr Octyl-Trichthoxy Silane, 4 phr Sorbitan Monooleate, and Insoluble Sulfur without Si69

Sample	8	9	10	11	12	13	14	15	16	17	C-C
Insoluble S (phr)	1.4	1.7	2	2.3	2.6	2.9	3.3	3.7	4.1	4.5	0
Total S (phr)	2.8	3.1	3.4	3.7	4	4.3	4.7	5.1	5.5	5.9	1.4
<b>Physical Test Results</b>											
ML <sub>1+4</sub> /100°C	84	81.9	80.7	78.9	78.5	103.6	101.8	99.5	99.8	101.7	75.7
<b>Monsanto Cure @ 171°C</b>											
ML	13.6	14.7	13.4	13	12.8	18	18.2	18	17.8	18.2	116
MH	33.4	34.8	37.1	37	38.3	46.5	48.3	50.6	50.8	53.9	37.37
ts2	2:54	2:48	2:41	2:47	2:44	2:42	2:34	2:30	2:28	2:29	2:30
ts90	10:51	9:50	9:42	9:28	9:15	12:05	11:36	11:11	10:29	11:11	10:01
<b>Ring Tensile @ 24°C</b>											
100 % Modulus, psi	188	184	209	194	227	212	267	256	284	326	313
300 % Modulus, psi	494	485	592	556	667	670	792	765	872	988	1150
Tensile str, psi	1798	1550	1814	1548	1769	1842	2120	1757	1925	2076	2809
% Elongation	724	657	641	613	594	601	591	538	527	510	556
Break energy, lbs/in <sup>2</sup>	5273	4203	4835	4000	4445	4569	5196	4034	4343	4580	6596

TABLE IV CONTINUED

Sample	8	9	10	11	12	13	14	15	16	17	C
Ring Tensile @ 100°C											
100% Modulus, psi	131	151	191	215	187	210	231	255	286	292	268
300% Modulus, psi	333	381	519	566	532	621	656	730	846	833	661
Tensile str, psi	905	1062	1233	1162	983	1156	1017	878	1079	1042	1263
% Elongation	649	652	592	529	500	500	441	340	375	364	364
Break Energy, lbs/in <sup>2</sup>	2612	3070	3306	2850	2310	2849	2172	1565	1984	1906	2092
Ring Tear @ 171°C, ppi	250	217	228	230	201	247	216	201	192	221	276
Pendulum Rebound 65°C	33.6	35	32.4	37.6	40.2	37.2	40.2	37.6	41.2	41.4	53.6
Wet Stanley London, (#/std)	56/53	54/53	56/53	53/53	57/53	60/54	62/54	63/54	64/54	63/54	
Shore A @ 24°C	68	67	68	68	69	71	71	73	73	72	65
Dispersion Index #1	85.6	85.5	86.5	87.1	88						59.4
Specific Gravity	1.184	1.186	1.189	1.188	1.189	1.195	1.197	1.199	1.199	1.21	1.202
Rheometrics @ 7% strain											
tan $\delta$ @ 65°C	.1978	.1924	.1807	.1858	.1789	.1697	.1662	.158	.1583	.1503	.1839
$\Delta G'$ @ 65°C, MPa	4.884	6.201	6.133	5.937	6.117	7.747	8.845	9.295	9.552	10.041	6.83
Tensile Retraction											
Mc x 10 <sup>-3</sup> g/mol	20.9	20.0	17.5	17.4	16.3	15.4			13.2	12.3	12.2

A further series of tests were conducted, in which, Formulation B, described in Table III, was processed with added sulfur and a processing aid comprising 1.5 phr octyl-triethoxy silane, 0.5 phr Si69, and 4 phr sorbitan olcate. Test conditions and results are reported for Examples 18 - 22 in Table V, below.

TABLE V

Physical Properties of Formulation B with 1.5 phr Octyl-triethoxysilane, 4 phr Sorbitan, 0.5 Si69 and Insoluble Sulfur					
Sample	18	19	20	21	22
Insoluble S (phr)	2.8	3.2	3.6	4	4.4
Total S (phr)	4.2	4.6	5	5.4	5.8
Physical Test Results					
ML <sub>1+4</sub> /100°C	81.9	83.6	84.2	86.3	80.8
Monsanto Cure @ 171°C					
ML	13.15	13.2	13.15	13.82	12.48
MH	41.84	44.62	44.62	46.58	46.98
ts2	2:50	2:44	2:43	2:35	2:38
tc90	10:15	10:12	9:12	9:24	8:59
Ring Tensile @ 24°C					
100 % Modulus, psi	273	291	326	341	408
300 % Modulus, psi	935	994	1112	1158	1452
Tensile str, psi	2323	2183	2112	2012	2497
% Elongation	582	537	483	461	460
Break Energy, lbs/in <sup>2</sup>	5760	5099	4545	4164	5130
Ring Tensile @ 100°C					
100 % Modulus, psi	251	251	287	307	311
300 % Modulus, psi	826	798	933	1030	998
Tensile str, psi	1326	1215	1255	1229	1113
% Elongation	444	428	388	350	329
Break Energy, lbs/in <sup>2</sup>	2720	2439	2306	2069	1800
Ring Tear @ 171°C, psi	240	230	201	219	206
Pendulum Rebound 65°C	37.2	39	42.8	39.4	42.4
Wet Stanley London (#/std)	64/53	61/53	64/53	65/53	65/53
Shore A, @ RT	72	71	72	74	73
Specific Gravity	1.195	1.196	1.197	1.197	1.202
Rheometries @ 7 % strain					
tan $\delta$ @ 65°C	0.1577	0.1528	0.1444	0.1384	0.1533
$\Delta G'$ @ 65°C, MPa	6.89	6.798	6.676	6.285	7.789
Tensile Retraction Mc, x 10 <sup>-3</sup> g/mol	12.6	12.4	11.1	10.4	9.7

The present invention can thus further utilize the presence of an ester of a fatty acid or an ester of a polyol as a processing aid to replace the silane Si69 to give equal processability of the vulcanizable compound, and better hot tear strength and lower hysteresis of the vulcanized rubber stock, without loss of the other measured physical properties.

The further processing aid, such as the preferred sorbitan oleate, is air stable and does not decompose. The sorbitan oleate is lower in cost and more storage stable than Si69, and when used with a silica filler and a silane terminated polymer, gives similar reduction of ML<sub>4</sub>, and tan  $\delta$  with an increase in tear strength.

The additional processing aids useful according to the present invention include esters of fatty acids or esters of polyols. Representative examples include the sorbitan oleates, such as sorbitan monooleate, dioleat , trioleate and sesquioleate, as well as sorbitan esters of laurate, palmate and stearate fatty acids, and the polyoxyethylene derivatives of each, and other polyols, including glycols such as polyhydroxy compounds and the like. Of these, sorbitan monooleate is preferred.

It is therefore demonstrated that the present invention provides a means for improving the processability of formulations of diene polymer elastomers with silica-filler, reducing the viscosity of silica-filled elastomeric vulcanizable compounds. It is further demonstrated that the present invention provides vulcanizable silica-filled elastomeric compounds having enhanced physical properties.

It should be appreciated that the present invention is not limited to the specific embodiments described above, but includes variations, modifications and equivalent embodiments defined by the following claims.

### Claims

1. A process for the preparation of a silica-filled, vulcanized elastomeric compound comprising:
  - mixing an elastomer with an amorphous silica filler, 0 to less than about 1 % by weight based on said silica filler of bis[3-(triethoxysilyl)propyl]tetrasulfide, an alkylalkoxysilane and a cure agent; and, effecting vulcanization.
2. The process as in claim 1 wherein the elastomer is a diene monomer homopolymer or a copolymer of a diene monomer and a monomer selected from the group consisting of monovinyl aromatic monomers and triene monomers.
3. The process as in claim 1 wherein the alkylalkoxysilane is represented by the formula  $(R_1)_2Si(OR_2)_2$  or  $R_1Si(OR_2)_3$ ,
  - wherein each  $R_1$  independently is selected from the group consisting of C1 to about C18 aliphatic, about C6 to about C12 cyclo-aliphatic, and about C6 to about C18 aromatic; and,
  - wherein the alkoxy groups are the same or are different, each  $R_2$  independently containing from one to about 6 carbon atoms.
4. The process as in claim 1 wherein the alkylalkoxysilane is represented by the formula  $(R_1)_2Si(OR_2)_2$  or  $R_1Si(OR_2)_3$ ,
  - wherein each  $R_1$  independently is selected from the group consisting of C1 to about C10 aliphatic, about C6 to about C10 cyclo-aliphatic, and about C6 to about C12 aromatic; and,
  - wherein the alkoxy groups are the same or are different, each  $R_2$  independently containing from one to about 6 carbon atoms.
5. The process as in claim 1 wherein the alkylalkoxysilane is selected from the group consisting of octyltriethoxy silane, octyltrimethoxy silane, (3-glycidoxypropyl)trimethoxy silane, (3-glycidoxypropyl)triethoxy silane, hexyltrimethoxy silane, ethyltrimethoxy silane, propyltriethoxy silane, phenyltrimethoxy silane, cyclohexyltrimethoxy silane, cyclohexyltriethoxy silane, dimethyldimethoxy silane, 3-chloropropyltriethoxy silane, methacryltrimethoxy silane, and i-butyltriethoxy silane.
6. The process as in claim 1 wherein the alkylalkoxysilane is octyltriethoxysilane.
7. The process as in claim 1, including mixing prior to vulcanizing, a processing aid comprising at least one of an ester of a fatty acid or an ester of a polyol.
8. The process as in claim 7 wherein the processing aid is selected from the group consisting of at least one sorbitan ester of an oleate, laurate, palmate and stearate fatty acids, polyoxyethylene derivatives thereof, at least one ester of a polyhydroxy compound, and mixtures thereof.
9. The process as in claim 7 wherein the processing aid is sorbitan monooleate.
10. The process as in claim 1 wherein the elastomer is styrene butadiene rubber.
11. The process as in claim 1 wherein the elastomer is a copolymer of styrene butadiene rubber and butyl rubber.

12. The process as in claim 1 including mixing the elastomer with carbon black.
13. The process as in claim 1 including mixing insoluble sulfur prior to vulcanizing.
- 5 14. A vulcanizable silica-filled compound comprising an elastomer, a silica filler, from 0 to less than about 1 % by weight based on said silica filler of bis[3-(triethoxysilyl)propyl]tetrasulfide, an alkylalkoxysilane and a cure agent.
15. The compound as in claim 14 wherein the alkylalkoxysilane is represented by the formula  $(R_1)_2Si(OR_2)_2$  or  $R_1Si(OR_2)_3$ ,  
 10        wherein each  $R_1$  independently is selected from the group consisting of C1 to about C18 aliphatic, about C6 to about C12 cyclo-aliphatic, and about C6 to about C18 aromatic; and,  
          wherein the alkoxy groups are the same or are different, each  $R_2$  independently containing from one to about 6 carbon atoms.
- 15 16. The compound as in claim 14 wherein the alkylalkoxysilane is represented by the formula  $(R_1)_2Si(OR_2)_2$  or  $R_1Si(OR_2)_3$ ,  
          wherein each  $R_1$  independently is selected from the group consisting of C1 to about C10 aliphatic, about C6 to about C10 cyclo-aliphatic, and about C6 to about C12 aromatic; and,  
          wherein the alkoxy groups are the same or are different, each  $R_2$  independently containing from one to  
 20        about 6 carbon atoms.
17. The compound as in claim 14 wherein the alkylalkoxysilane is selected from the group consisting of octyltriethoxy silane, octyltrimethoxy silane, (3-glycidoxypentyl)trimethoxy silane, (3-glycidoxypentyl)triethoxy silane, hexyltri-  
 25        methoxy silane, ethyltrimethoxy silane, propyltriethoxy silane, phenyltrimethoxy silane, cyclohexyltrimethoxy silane, cyclohexyltriethoxy silane, dimethyldimethoxy silane, 3-chloropropyltriethoxy silane, methacryloxytrimethoxy silane, and i-butyltriethoxy silane.
18. The compound as in claim 14 wherein the alkylalkoxysilane is octyltriethoxysilane.
- 30 19. The compound as in claim 14, including a processing aid comprising at least one of an ester of a fatty acid or an ester of a polyol.
20. The compound as in claim 19 wherein the processing aid is selected from the group consisting of at least one sorbitan ester of an oleate, laurate, palmate and stearate fatty acid, their polyoxyethylene derivatives, at least one ester  
 35        of a polyhydroxy compound, and mixtures thereof.
21. The compound as in claim 19 wherein the processing aid is sorbitan monooleate.
22. The compound of claim 14 wherein the elastomer is a diene monomer homopolymer or a copolymer of at least one  
 40        diene and at least one monomer selected from the group consisting of monovinyl aromatic monomers and triene monomers.
23. The compound of claim 22 wherein the elastomer is styrene butadiene rubber.
- 45 24. The compound as in claim 23 wherein the elastomer is a copolymer of styrene butadiene rubber and butyl rubber.
25. The compound of claim 14 further containing a carbon black filler.
26. The compound of claim 14 further containing a natural rubber.
- 50 27. The compound of claim 19 further containing a carbon black filler.
28. The compound of claim 19 further containing a natural rubber.
- 55 29. A pneumatic tire comprising tread stock vulcanized from the vulcanizable silica-filled compound of claim 14.
30. A pneumatic tire comprising tread stock vulcanized from the vulcanizable silica-filled compound of claim 19.



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 98 11 2481

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	DE 43 08 311 A (DEGUSSA) 22 September 1994  * abstract; claims; examples * * page 2, line 24 - line 36 * ---	1-6, 10, 11, 13-18, 22-24, 26	C08K5/54 C08K5/10 C08K3/36 C08L21/00
X	US 4 436 847 A (WAGNER MELVIN P) 13 March 1984  * abstract; claims; examples * * column 5, line 19 - line 51 * * column 8, line 9 - line 62 * ---	1-6, 10, 11, 13-18, 22-24, 26, 29	
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P, X	EP 0 795 577 A (GOODYEAR TIRE & RUBBER) 17 September 1997  * abstract; claims; example III; tables 4-6 * -----	1-6, 10-18, 22-26, 29	
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>15 October 1998</b>	Examiner <b>Mettler, R-M</b>
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... Δ : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03/82 (P04C01)



US006080835A

**United States Patent** [19]

Lawson et al.

[11] Patent Number: **6,080,835**[45] Date of Patent: **Jun. 27, 2000**[54] **AMINOALKYLLITHIUM COMPOUNDS  
CONTAINING CYCLIC AMINES AND  
POLYMERS THEREFROM**[75] Inventors: **David F. Lawson**, Uniontown; **Thomas A. Antkowiak**, Wadsworth; **James E. Hall**, Mogadore; **Mark L. Stayer, Jr.**, Suffield; **John R. Schreffler**, Clinton, all of Ohio[73] Assignee: **Bridgestone Corporation**, Tokyo, Japan

[\*] Notice: This patent issued on a continued prosecution application filed under 37 CFR 1.53(d), and is subject to the twenty year patent term provisions of 35 U.S.C. 154(a)(2).

This patent is subject to a terminal disclaimer.

[21] Appl. No.: 08/936,364

[22] Filed: Sep. 24, 1997

**Related U.S. Application Data**

[63] Continuation of application No. 08/813,703, Mar. 7, 1997, Pat. No. 5,785,778, which is a continuation of application No. 08/658,242, Jun. 4, 1996, Pat. No. 5,610,237, which is a division of application No. 08/382,358, Feb. 1, 1995, Pat. No. 5,574,109.

[51] Int. Cl.<sup>7</sup> ..... **C08G 61/00**[52] U.S. Cl. .... **528/396; 528/406; 528/417; 528/422; 528/423**[58] Field of Search ..... **528/396, 406, 528/417, 422, 423**[56] **References Cited****U.S. PATENT DOCUMENTS**

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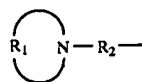
Primary Examiner—Robert Dawson

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[57] **ABSTRACT**

A functionalized polymer according to the invention includes a polymer molecule having the general formula AYLi where A is a cyclic amine-containing radical having the general formula

wherein R<sub>1</sub> is a divalent alkylene, an oxy- or amino-alkylene, or substituted alkylene having from 6 to about 20 carbon atoms; R<sub>2</sub> is a linear-, branched-, or cyclo-alkylene having from about 2 to about 20 carbon atoms; and Y is a divalent polymer radical and Li is a lithium atom bonded to a carbon atom of Y.**12 Claims, No Drawings**

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# AMINOALKYLLITHIUM COMPOUNDS CONTAINING CYCLIC AMINES AND POLYMERS THEREFROM

This application is a continuation of application Ser. No. 08/813,703, filed Mar. 7, 1997 now U.S. Pat. No. 5,785,778, which is a continuation of application Ser. No. 08/658,242, filed Jun. 4, 1996 now U.S. Pat. No. 5,610,237, which is a divisional of application Ser. No. 08/382,358, filed Feb. 1, 1995, now U.S. Pat. No. 5,574,109, issued Nov. 12, 1996.

## TECHNICAL FIELD

The subject invention relates to polymers made by anionic initiation with alkyllithium compounds containing cyclic amines, such as polymerizations of dienes and diene/ comonomer mixtures resulting in diene polymer and copolymer elastomers. Polymers prepared with the compounds of the present invention exhibit improved characteristics such as for example, improved hysteresis loss characteristics, and reproducible, relatively narrow range molecular weight distributions.

## BACKGROUND ART

When conducting polymerizations on a commercial basis, it is important to utilize process conditions and components which will allow the molecular weight of (the end products to be narrowly and reproducibly defined. The characteristics of a given polymer and its usefulness, are dependent, among other things, upon its molecular weight. Hence, it is desirable to be able to predict with some certainty the molecular weight of the end product of the polymerization. When the molecular weight is not narrowly definable, or is not reproducible on a systematic basis, the process is at a commercial disadvantage.

Further, it is desirable to produce elastomeric compounds exhibiting improved characteristics such as reduced hysteresis loss characteristics. Such elastomers, when compounded to form articles such as tires, power belts and the like, will show an increase in rebound, a decrease in rolling resistance and less heat build-up when mechanical stresses are applied.

A major source of hysteretic power loss has been established to be due to the section of the polymer chain from the last cross link of the vulcanizate to the end of the polymer chain. This free end cannot be involved in an efficient elastic recovery process, and as a result, any energy transmitted to this section of the cured sample is lost as heat. It is known in the art that this type of mechanism can be reduced by preparing higher molecular weight polymers which will have fewer end groups. However, this procedure is not useful because processability of the rubber with compounding ingredients and during shaping operations decreases rapidly with increasing molecular weight of the rubber.

The present invention provides polymers made by anionic initiation with novel alkyl lithium compounds containing cyclic amines. Use of the compounds of the present invention allows the incorporation of a functionality from the initiator to be incorporated at least at the head of the polymer chain. The initiators used in the invention not only provide for improved polymerizations, but also result in polymers having a relatively predictable, controllable and reproducible molecular weight range distribution. Because of the incorporated functionality, the polymers and products of the invention exhibit improved (that is, reduced) hysteresis loss characteristics.

Certain aminoalkyllithium compounds are known in the art. For example, U.S. Pat. No. 4,935,471 discloses dialky-

lamino oligoalkenyl lithiums including piperidinyllithium and pyrrolidinyl oligoalkenyl lithiums. It has been found that when compounded with conventional vulcanizable rubber components, some of these materials do not interact effectively with carbon black. Others possess an odor which makes their commercial use undesirable. The present invention provides polymers derived from aminoalkyllithium compounds with improved interaction with carbon black and which do not have the objectionable odor associated with the piperidinyllithium and pyrrolidinyl compounds.

## DISCLOSURE OF THE INVENTION

It is therefore, an object of the present invention to provide polymers formed by anionic polymerization initiators.

It is a further object of the invention to provide a polymerization initiator which using such to initiate a polymerization will reproducibly result in a polymer within a narrow, predictable molecular weight range.

It is an additional object of the invention to provide a polymerization initiator which using such to initiate a polymerization will allow for the incorporation of a functional group at both the head and tail of the resulting polymer.

It is another object of the present invention to provide elastomers formed with such a polymerization initiator.

It is yet another object of the present invention to provide elastomers having a plurality of polymer molecules wherein substantially each molecule has a functional group from the initiator.

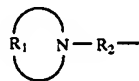
It is also an object of certain embodiments of the present invention to provide diene polymers and copolymers having reduced hysteresis characteristics.

It is a further object of the present invention to provide vulcanizable elastomeric compounds.

Still another object of the present invention is to provide an improved tire formed from an elastomer as described hereinabove.

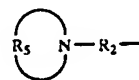
At least one or more of these objects together with the advantages thereof over the existing art, which shall become apparent from the specification which follows, are accomplished by the invention as hereinafter described and claimed.

In general, according to the invention, a functionalized polymer comprises a polymer molecule having the general formula  $AYLi$  where A is a cyclic amine-containing radical having the general formula (I)



wherein  $R_1$  and  $R_2$  are as discussed hereinabove; and Y is a divalent polymer radical.

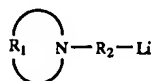
A functionalized polymer according to the present invention also comprises a polymer molecule having the general formula  $AYLi$  where A is a cyclic amine-containing radical having the general formula



wherein A,  $R_2$ ,  $R_3$  and Y are as discussed hereinabove.

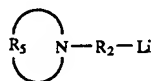
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There is also provided according to the invention a method of preparing a polymer which comprises preparing a solution of 1 or more anionically polymerizable monomers in a solvent; and, polymerizing under effective conditions, the monomers in the presence of a polymerization initiator having the general formula



wherein  $\text{R}_1$  and  $\text{R}_2$  are as discussed hereinabove.

A method for preparing a polymer according to the present invention comprises preparing a solution of 1 or more anionically polymerizable monomers in a solvent; and polymerizing under effective conditions, the monomers in the presence of a polymerization initiator having the general formula

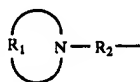


wherein  $\text{R}_2$  and  $\text{R}_3$  are as discussed hereinabove.

#### PREFERRED EMBODIMENT FOR CARRYING OUT THE INVENTION

As will become apparent from the description which follows, the present invention employs novel aminoalkyllithium compounds useful for example, as anionic polymerization initiators for the preparation of diene polymer and copolymer elastomers. It has been discovered herein that certain vulcanizable elastomeric compounds and articles thereof based upon such polymers formed using such initiators, exhibit useful properties, such as for example, reproducible relatively narrow molecular weight ranges. Furthermore, such polymers also contain a functionality from the initiator, which functionality is useful for example, in reducing hysteresis loss characteristics in the resulting polymers.

The preferred aminoalkyllithium compound used as anionic initiators in the invention contains a cyclic amine. The preferred initiator is therefore, an amine having the general formula  $\text{ALi}$ , wherein the component "A" represents the cyclic amine functionality to be incorporated at the initiation site or the head of the resulting polymer when the inventive amine compound is employed as an initiator. "A" is preferably a cyclic amine radical having the general formula (I)

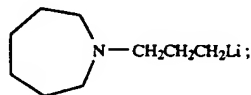


wherein  $\text{R}_1$  is a divalent alkylene, oxy- or amino-alkylene, or substituted alkylene moiety having from 6 to about 20 carbon atoms, more preferably from 6 to 12 carbon atoms; and,  $\text{R}_2$  is a linear-, branched-, or cyclo-alkylene moiety having from about 2 to about 20 carbon atoms, and more preferably, from 3 to 12 carbon atoms. The lithium atom, Li, is bonded directly to a carbon atom of A.

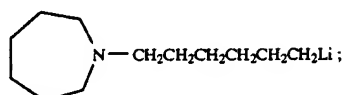
Examples of  $\text{R}_1$  include hexamethylene, heptamethylene, dodecamethylene and hexadecamethylene moieties and the

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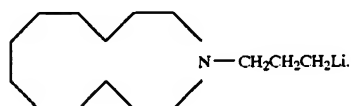
like. Examples of preferred  $\text{R}_2$  groups have from about 3 to about 6 carbon atoms and include propyl and hexyl moieties and the like. Hence, examples of preferred cyclic amino compounds according to the invention include hexamethyleneiminopropyllithium,



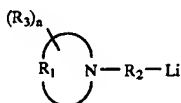
hexamethyleneiminohexyllithium,



and, dodecamethyleneiminopropyllithium



The carbon and nitrogen atoms in the cyclic amine ring structure of "A" can also be substituted, such that the aminoalkyllithium of this embodiment has the general formula



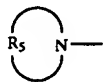
wherein  $\text{R}_3$  is a tertiary amino or an alkyl group having from about 1 to about 12 carbon atoms; an aryl having from about 6 to about 20 carbon atoms; an aralkyl having from about 7 to about 20 carbon atoms; an alkenyl having from about 2 to about 12 carbon atoms; a cycloalkyl having from about 5 to about 20 carbon atoms; a cycloalkenyl having from about 5 to about 20 carbon atoms; a bicycloalkyl having from about 6 to about 20 carbon atoms; or, a bicycloalkenyl having from about 6 to about 20 carbon atoms; where n is an integer of from about 1 to about 10. The O-, S- or N-containing analogs of  $\text{R}_3$ , which analogs are substantially non-reactive with the alkylithium of the cyclic amino compound, are also within the scope of the invention. By "analog" it is meant a compound in which one or more O, S and/or N atoms may replace one or more carbon atoms. The lithium atom, Li, is bonded directly to a carbon atom in  $\text{R}_2$ .

Further,  $\text{R}_2$  can be a branched- or cyclo-alkylene in addition to being a linear-alkylene as discussed hereinabove. Examples of branched-alkylene-containing (lithio)alkyl portions include 2,2-dimethylpropane-1,3-diyl; 2-methylpropane-1,3-diyl; 2-methylbutane-1,4-diyl; and 2,2-dimethyloctane-1,8-diyl. Examples of cyclo-alkylene (lithio)alkyl portions include cyclohexane-1,4-diyl; cyclohexane-1,3-diyl; cyclododecane-1,7-diyl; cyclooctane-1,3-diyl; and, cyclohexadecane-1,5-diyl.

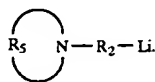
According to another embodiment of the present invention, the cycloalkyl amine portion of "A" has at least seven ring atoms therein, including about 2 to about 4 amine

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nitrogens. Such a cyclic amine compound has the general formula  $R_4R_2Li$  where  $R_2$  is as defined above, and  $R_4$  is a cyclic amino radical having the general formula



where  $R_5$  is selected from the group consisting of a divalent alkylene, an oxy- or amino-alkylene, and a substituted alkylene having from 4 to about 20 carbon atoms, a substituted nitrogen having the general formula  $R_6N$  where  $R_6$  is selected from the group consisting of an alkyl having from 1 to about 12 carbon atoms; a cycloalkyl having from about 5 to about 20 carbon atoms; an aryl having from about 6 to about 20 carbon atoms; and, an aralkyl having from 7 to about 20 carbon atoms; and mixtures thereof, with the limitation that  $R_4$  has from 2 to about 4 nitrogen atoms and a total of from 6 to about 24 atoms in the ring structure thereof. The cyclic amine initiator according to the invention can thus have the following general formula, where  $R_5$ ,  $R_2$  and  $Li$  are as described hereinabove:



The atoms in  $R_5$  can be substituted in the same manner as described above, that is, with "A" being substituted with  $(R_3)_n$ .

Therefore, in addition to formula (I) hereinabove, "A" can also be a cyclic amine radical having the general formula (II)  $R_4R_2\cdot$  where  $R_4$  and  $R_2$  are as described hereinabove.

Therefore, according to the present invention, in the alkyl lithium compounds containing cyclic amines, the size of the ring in the cyclic amine portion is greater than or equal to 7 atoms when there is only one nitrogen atom in the ring, or greater than or equal to 6 atoms when there are 2 or more nitrogen atoms in the ring.

Examples of amine compounds having the structure  $R_4R_2Li$  as above are mono-N alkyl or N-aryl derivatives or piperazines; mono-N-alkyl derivatives of homopiperazine (1,4-diazacycloheptanes); mono-N-alkyl derivatives of 1,4- or 1,5-diazacyclooctanes, and ring C-substituted 1,4- or 1,5-diazacyclooctanes and the like. Ring C-substituted N-alkylpiperazines are also within the scope of the invention. Substituted triaza ring systems are also included within  $R_4$ .

The initiator used in the present invention can be formed by any number of techniques. One preferred method of preparing a cyclic amine compound according to the invention is to react a cyclic aminoalkyl halide with a lithio reactant selected from elemental lithium metal, an organolithium compound, and mixtures thereof. The aminoalkyl halide has the general formula  $AX$  where  $A$  is as defined by formulas I or II hereinabove, and  $X$  is a halogen selected from bromine, chlorine, iodine or the like, preferably bromine or chlorine, and wherein  $X$  is bonded directly to a carbon atom of  $R_2$  in either formula I or II. The preparation of cyclic aminoalkyl halides is known to the art.

When reacted with elemental lithium metal in a suitable solvent such as hexane, cyclohexane, benzene or the like, the resulting reduction reaction produces a lithiated cyclic amine compound  $ALi$  where "A" is as defined hereinabove and the lithium atom,  $Li$ , is directly bonded to a carbon atom

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of A. The lithiated cyclic amine compound  $ALi$  can be complexed with one or more ligand molecules (such as THF) which help stabilize it but do not otherwise affect the reaction.

In the alternative, the amino reactant  $AX$  can also be reacted with an organolithium reactant having the general formula  $RLi$ , again in a suitable solvent such as those described hereinabove.  $RLi$  can be for example, selected from the group consisting of alkyls, cycloalkyls, alkenyls, aryls and aralkyls having from 1 to about 20 carbon atoms and short chain length low molecular weight polymers from diolefin and vinyl aryl monomers having up to about 25 units. Typical alkyls include n-butyl, s-butyl, t-butyl, methyl, ethyl, isopropyl and the like. The cycloalkyls include cyclohexyl, menthyl and the like. The alkenyls include allyl, vinyl and the like. The aryl and aralkyl groups include phenyl, benzyl, oligo(styryl) and the like. Exemplary short chain length polymers include the oligo(butadienyls), oligo(isoprenyls), oligo(styryls) and the like. Alkyl lithium reactants such as t-butyl lithium are preferred.

The two components are allowed to react for up to about twenty-four hours at low to ambient temperature ( $-70^\circ$  to  $30^\circ$  C.), or elevated temperatures up to about  $100^\circ$  C., preferably at less than  $50^\circ$  C., and more preferably at less than  $38^\circ$  C.

If one atom equivalent of lithium in the organolithium reactant is used per atom equivalent of  $AX$ , a byproduct of the reaction will be an organo halide (that is,  $RX$ ) which may be undesirable for the intended use of the inventive compound. It may therefore, be preferable to employ two or more atom equivalents of lithium from the organolithium reactant per atom equivalent of  $AX$ . It is believed that a reaction with the excess of lithium will result in a lithium halide and other low molecular weight hydrocarbon by-products, which may be more acceptable for the intended use of the inventive initiator material.

As stated above, the compound  $ALi$  or  $R_4R_2Li$  thus formed may be employed as an initiator to prepare any anionically-polymerized elastomer, e.g., polybutadiene, polyisoprene and the like, and copolymers thereof with monovinyl aromatics such as styrene, alpha methyl styrene and the like, or trienes such as myrcene. Thus, the elastomers include diene homopolymers and copolymers thereof with monovinyl aromatic polymers. Suitable monomers include conjugated dienes having from about 4 to about 12 carbon atoms and monovinyl aromatic monomers having 8 to 18 carbon atoms and trienes. Examples of conjugated diene monomers and the like useful in the present invention include 1,3-butadiene, isoprene, 1,3-pentadiene, 2,3dimethyl-1,3-butadiene and 1,3-hexadiene, and aromatic vinyl monomers include styrene, alpha-methylstyrene, p-methylstyrene, vinyltoluene and vinylnaphthalene. The conjugated diene monomer and aromatic vinyl monomer are normally used at the weight ratios of 95-50:5-50, preferably 95-65:5-35.

Polymerization is conducted in polar or non-polar solvent, such as tetrahydrofuran (THF), a hydrocarbon solvent, such as the various cyclic and acyclic hexanes, heptanes, octanes, pentanes, their alkylated derivatives, and mixtures thereof. In order to promote randomization in copolymerization and to control vinyl content, a polar coordinator may be added to the polymerization ingredients. Amounts range between 0 and 90 or more equivalents per equivalent of lithium. The amount depends on the amount of vinyl desired, the level of styrene employed and the temperature of the polymerization, as well as the nature of the specific polar coordinator (modifier) employed. Suitable polymerization

modifiers include for example, ethers or amines to provide the desired microstructure and randomization of the comonomer units. The molecular weight of the polymer ("base polymer") that is produced in this invention is optimally such that a proton-quenched sample will exhibit a gum Mooney (ML/4/100) of from about 1 to about 150. However, useful lower molecular weight compounds can also be made using these initiators. These might typically be considered fluids, having molecular weights ranging from several hundreds to tens of thousands of mass units.

Other compounds useful as polar coordinators are organic and include tetrahydrofuran (THF), linear and cyclic oligomeric oxolanyl alkanes such as 2,2-bis(2'-tetrahydrofuryl) propane, di-piperidyl ethane, dipiperidyl methane, hexamethylphosphoramide, N-N'-dimethylpiperazine, diazabicyclooctane, dimethyl ether, diethyl ether, tributylamine and the like. The linear and cyclic oligomeric oxolanyl alkane modifiers are described in U.S. Pat. No. 4,429, 091, owned by the Assignee of record, the subject matter of which relating to such modifiers is incorporated herein by reference. Compounds useful as polar coordinators include those having an oxygen or nitrogen hetero-atom and a non-bonded pair of electrons. Other examples include dialkyl ethers of mono and oligo alkylene glycols; "crown" ethers; tertiary amines such as tetramethylethylenediamine (TMEDA); linear THF oligomers; and the like.

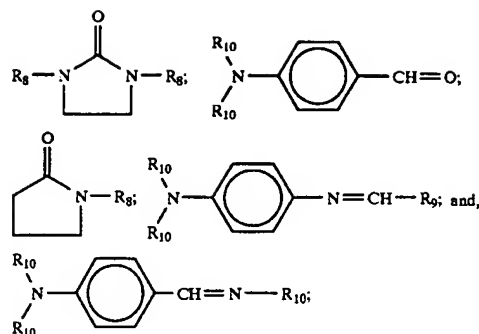
A batch polymerization is begun by charging a blend of monomer(s) and normal alkane solvent to a suitable reaction vessel, followed by the addition of the polar coordinator (if employed) and the initiator compound previously described. The reactants are heated to a temperature of from about 20 to about 200° C., and the polymerization is allowed to proceed for from about 0.1 to about 24 hours. A functional amine group is derived from the initiator compound and attaches at the initiation site. Thus, substantially every resulting polymer molecule can be represented by the following general formula



where A is as described above, and Y is a divalent polymer radical which is derived from any of the foregoing diene homopolymers, monovinyl aromatic polymers, diene/monovinyl aromatic random copolymers and block copolymers. The monomer addition at the lithium end causes the molecular weight of the polymer to increase as the polymerization continues.

To terminate the polymerization, and thus further control polymer molecular weight, a terminating agent, coupling agent or linking agent may be employed, all of these agents being collectively referred to herein as "terminating reagents". Certain of these reagents may provide the resulting polymer with a multifunctionality. That is, the polymers initiated according to the present invention, may carry at least one amine functional group A as discussed hereinabove, and may also carry a second functional group selected and derived from the group consisting of terminating reagents, coupling agents and linking agents.

Useful terminating, reagents include active hydrogen compounds such as water or alcohol; carbon dioxide; N,N, N',N'-tetradialkyldiamino-benzophenone (such as tetramethyldiaminobenzophenone or the like); N,N-dialkylaminobenzaldehyde (such as dimethylaminobenzaldehyde or the like); 1,3-dialkyl-2-imidazolidinones (such as 1,3-dimethyl-2-imidazolidinone or the like); 1-alkyl substituted pyrrolidinones; 1-aryl substituted pyrrolidinones; dialkyl- and dicycloalkyl-carbodiimides having from about 5 to about 20 carbon atoms; (R<sub>7</sub>)<sub>2</sub>ZX<sub>b</sub>;



where Z is tin or silicon. It is preferred that Z is tin.

R<sub>7</sub> is an alkyl having from about 1 to about 20 carbon atoms; a cycloalkyl having from about 3 to about 20 carbon atoms; an aryl having from about 6 to about 20 carbon atoms; or, an aralkyl having from about 7 to about 20 carbon atoms. For example, R<sub>7</sub> may include methyl, ethyl, n-butyl, neophyl, phenyl, cyclohexyl or the like.

X is chlorine or bromine, "a" is from 0 to 3, and "b" is from about 1 to 4; where a+b=4.

Each R<sub>8</sub> is the same or different and is an alkyl, cycloalkyl or aryl, having from about 1 to about 12 carbon atoms. For example, R<sub>8</sub> may include methyl, ethyl, nonyl, t-butyl, phenyl or the like.

R<sub>9</sub> is an alkyl, phenyl, alkylphenyl or dialkylaminophenyl, having from about 1 to about 20 carbon atoms. For example, R<sub>9</sub> may include 1-butyl, 2-methyl-4-pentene-2-yl, phenyl, p-tolyl, p-butylphenyl, p-dodecylphenyl, p-diethyl-aminophenyl, p-(pyrrolidino)phenyl, and the like.

Each R<sub>10</sub> is the same or different, and is an alkyl or cycloalkyl having from about 1 to about 12 carbon atoms. Two of the R<sub>10</sub> groups may together form a cyclic group. For example, R<sub>10</sub> may include methyl, ethyl, octyl, tetramethylene, pentamethylene, cyclohexyl or the like.

R<sub>11</sub> may include alkyl, phenyl, alkylphenyl or dialkylaminophenyl, having from about 1 to about 20 carbon atoms. For example, R<sub>11</sub> may include methyl, butyl, phenyl, p-butylphenyl, p-nonylphenyl, p-dimethylaminophenyl, p-diethylaminophenyl, p-(piperidino)phenyl, or the like.

Other examples of useful terminating reagents include tin tetrachloride, (R<sub>11</sub>)<sub>3</sub>SnCl, (R<sub>11</sub>)<sub>2</sub>SnCl<sub>2</sub>, R<sub>11</sub>SnCl<sub>3</sub>, carbodiimides, N-methylpyrrolidine, cyclic amides, cyclic ureas, isocyanates, Schiff bases, 4,4'-bis(diethylamino)benzophenone, and the like, where R<sub>11</sub> is an alkyl, cycloalkyl or aralkyl having from 1 to about 12 carbon atoms, and other reactive hysteresis-reducing terminating compounds which may contain other heteroatoms such as oxygen, nitrogen, sulfur, phosphorus, tin, noninterfering halogen, etc. Suitable terminating reagents also include the isomeric vinylpyridines, dialkylaminobenzaldehydes, (bis) dialkylaminobenzophenones (Michler's ketones), dimethylimidazolidinone, etc. The living polymer may also be coupled with any of the various known coupling reagents, such as silicon tetrachloride, etc., to prepare symmetrically "dicapped" polymers. By the end-linking of polymers initiated with lithium hydrocarbon amides, through reaction with for example, R<sub>a</sub>SnY<sub>b</sub>, where R, Y, a and b are as described hereinabove; SnCl<sub>4</sub>; or C<sub>4</sub>H<sub>9</sub>SnCl<sub>3</sub>; to obtain products with substantially greater than 10 percent end-linking through tin, especially desirable elastomeric compositions with low hysteresis properties are prepared.

The terminating reagent is added to the reaction vessel, and the vessel is agitated for about 1 to about 1000 minutes. As a result, an elastomer is produced having an even greater affinity for compounding materials such as carbon black, and hence, even further reduced hysteresis. Additional examples of terminating reagents include those found in U.S. Pat. No. 4,616,069 which is herein incorporated by reference for the disclosure of terminating agents.

The polymer may be separated from the solvent by conventional techniques. These include steam or alcohol coagulation, thermal desolventization, or any other suitable method. Additionally, solvent may be removed from the resulting polymer by drum drying, extruder drying, vacuum drying or the like.

The elastomers made from the anionic initiators of the present invention comprise a plurality of polymer molecules, having a functional group at both the head, and preferably also, at the tail of the resulting polymer. Compounding such elastomers results in products exhibiting reduced hysteresis, which means a product having increased rebound, decreased rolling resistance and has less heat build-up when subjected to mechanical stress.

The polymers made from the anionic initiators of the present invention can be used alone or in combination with other elastomers to prepare a product such as a tire treadstock, sidewall stock or other tire component stock compound. Such stocks are useful for forming tire components such as treads, subreads, black sidewalls, body ply skims, bead fillers and the like. At least one such component is produced from a vulcanizable elastomeric or rubber composition. For example, they can be blended with any conventionally employed treadstock rubber which includes natural rubber, synthetic rubber and blends thereof. Such rubbers are well known to those skilled in the art and include synthetic polyisoprene rubber, styrene/butadiene rubber (SBR), polybutadiene, butyl rubber, poly(chloroprene), ethylene/propylene rubber, ethylene/propylene/diene rubber (EPDM), acrylonitrile/butadiene rubber (NBR), silicone rubber, the fluoroclastomers, ethylene acrylic rubber, ethylene vinyl acetate copolymer (EVA), epichlorohydrin rubbers, chlorinated polyethylene rubbers, chlorosulfonated polyethylene rubbers, hydrogenated nitrile rubber, tetrafluoroethylene/propylene rubber and the like. When the polymers of the present invention are blended with conventional rubbers, the amounts can vary widely such as between 10 and 99 percent by weight.

The polymers can be compounded with carbon black in amounts ranging from about 20 to about 100 parts by weight, per 100 parts of rubber (phr), with about 40 to about 70 phr being preferred. The carbon blacks may include any of the commonly available, commercially-produced carbon blacks but those having a surface area (EMSA) of at least 20 m<sup>2</sup>/g and more preferably at least 35 m<sup>2</sup>/g up to 200 m<sup>2</sup>/g or higher are preferred. Surface area values used in this application are those determined by ASTM test D-1765 using the cetyltrimethyl-ammonium bromide (CTAB) technique. Among the useful carbon blacks are furnace black, channel blacks and lamp blacks. More specifically, examples of the carbon blacks include super abrasion furnace (SAF) blacks, high abrasion furnace (HAF) blacks, fast extrusion furnace (FEF) blacks, fine furnace (FF) blacks, intermediate super abrasion furnace (ISAF) blacks, semi-reinforcing furnace (SRF) blacks, medium processing channel blacks, hard processing channel blacks and conducting channel blacks. Other carbon blacks which may be utilized include acetylene blacks. Mixtures of two or more of the above blacks can be used in preparing the carbon black products of the invention.

Typical values for surface areas of usable carbon blacks are summarized in the following TABLE I.

TABLE I

CARBON BLACKS	
ASTM Designation (D-1765-82a)	Surface Area (m <sup>2</sup> /g) (D-3765)
N-110	126
N-220	111
N-339	95
N-330	83
N-550	42
N-660	35

The carbon blacks utilized in the preparation of the rubber compounds used may be in pelletized form or an unpelletized flocculent mass. Preferably, a for more uniform mixing, unpelletized carbon black is preferred. The reinforced rubber compounds can be cured in a conventional manner with known vulcanizing agents at about 0.5 to about 4 phr. For example, sulfur or peroxide-based curing systems may be employed. For a general disclosure of suitable vulcanizing agents one can refer to Kirk-Othmer, *Encyclopedia of Chemical Technology* 3rd ed., Wiley Interscience, N.Y. 1982, Vol. 20, pp. 365-468, particularly "Vulcanization Agents and Auxiliary Materials" pp. 390-402. Vulcanizing agents may be used alone or in combination.

Vulcanizable elastomeric compositions made from the above elastomers can be prepared by compounding or mixing the polymers thereof with carbon black and other conventional rubber additives such as fillers, plasticizers, antioxidants, curing agents and the like, using standard rubber mixing equipment and procedures and conventional amounts of such additives.

#### GENERAL EXPERIMENTAL

In order to demonstrate the preparation and properties of the initiators according to the present invention and their use in anionic polymerization, a number of such cyclic amino alkyl lithium compounds were prepared. These compounds were then used as initiators to form a number of elastomers.

The aminoalkyllithium reagents of the invention may be prepared under a variety of conditions, using various hydrocarbon solvents as discussed hereinabove. The reagents may be used in polymerizations using such polar or nonpolar solvents as may be necessary for improved solubility of the aminoalkyllithium reagent, provided that the solvents are compatible with anionic polymerizations and the solvent recovery and polymer drying procedures.

In one preferred embodiment of the invention that provides for the production of reduced hysteresis polymers in substantially hydrocarbon solvents, such as hexane or cyclohexane, the initiator is hexamethyleneiminopropyllithium, which may be generated by at least two exemplary routes as is also discussed above: 1) by the reaction of a mixture of one equivalent of for example, 1-(N-hexamethyleneimino)-3-chloropropane with about two atom equivalents of lithium metal; or 2) a "one-pot" generation of for example, hexamethyleneiminopropyllithium, wherein 1-bromo-3-chloropropane is treated with N-lithiohexamethyleneimine, and the product 1-(N-hexamethyleneimino)-3-chloropropane is then treated *in situ* with two equivalents of t-butyllithium. The reactions are preferably performed in hexanes, cyclohexane, benzene, or mixtures thereof.

The amino alkyl lithium reagents of the invention may be formed in a solvent or solvent mixture, and then transferred to another solvent or solvent mixture for use in a polymerization reaction.

The initiators of this invention may optionally be treated with from about one to 500 equivalents of a monomer such as butadiene or isoprene, before the main (co) polymerization charge is made, although this is not required. Polymers according to the invention can be prepared with a relatively narrow molecular weight range distribution, with a substantial fraction of living C-Li chain ends adaptable to further functionalization or coupling, being obtained.

The initiator formation, polymerization, and coupling and/or termination may be performed in one reaction vessel, or second or third reactor vessels, or transfer lines from the original reactor can be used, by introducing the preformed initiator to the monomer mixture, or vice-versa. Polymerization and post-treatment conditions should be used that avoid the introduction of air and/or protic or other reactive contaminants, such as moisture, etc., and prolonged heating or storage at excessive temperatures should be avoided unless the live ends are stabilized. Low to high temperatures (from about -70° C. to about 200° C.) are useful for the polymerizations and the terminations. Polymerization and post-treatment temperatures of from about 15° C. to 125° C. are preferred. The polymerization time may vary from a few minutes to days, depending on the temperature, solvent and presence of any donor solvent, the monomer structures, and the molecular weight desired.

Any suitable method for isolation of the terminated rubber or fluid may be used, for example: quenching with water, steam, an acid or an alcohol (these may be introduced during the desolventization step), and desolventization by drum drying, coagulation in alcohol, water or steam, extruder drying, vacuum drying, spray drying or any combination thereof. Desolventization by drum-drying, coagulation in alcohol, steam or hot water desolventization, extruder drying, vacuum drying, spray drying or combinations thereof are preferred. An antioxidant and/or antiozonant compound is usually added to the polymer or polymer cement at or before this stage. In most of the experimental examples of this invention, alcohol coagulation followed by drum-drying or vacuum drying were used.

Upon drying, the elastomers are compounded in a carbon black-filled test stock (see Low-Oil Test Recipe, TABLE II), and the physical properties determined in comparison to those of related base polymers without the modifications. In practice, a wide variety of compounding recipes may be used to give favorable results with this invention, although hysteresis properties may vary from formulation to formulation, depending on the type and amount of carbon black and oil used, and so on. Certain other fillers, such as silica or hydrated silica may also be useful. Furthermore, the polymers made with the initiators of this invention may be combined in proportions of 20 to 100 percent by weight with 80 to 0 percent by weight of other polymers to give elastomeric compositions with reduced hysteresis loss characteristics. The low molecular weight products made from the initiators of this invention may be used at low levels to influence the properties of mixtures with other fluids and/or particulates.

TABLE II

LOW-OIL TEST FORMULATION  
FOR EVALUATION OF HYSTERESIS

Ingredient	Mix Order	Parts per Hundred Parts of Rubber
Polymer	1	100
Naphthenic oil	2	10
Carbon black, N-351	3	55
ZnO	4	3
Antioxidant	5	1
Wax blend	6	2
Total Masterbatch:		171
Stearic acid		2
Sulfur		1.5
Accelerator		1
Total Final:		175.5

Masterbatch: 145°-155° C., 60 RPM  
(drop after 5 min, @ 155°-175° C.)  
Final: 77°-95° C., 40 RPM

The following preparations exemplify the invention.

EXAMPLE 1. A "one-pot" preparation of  
hexamethyleneiminopropyllithium

The (bis)tetrahydrofuran N-lithio salt of hexamethyleneimine was prepared in hexane. Equimolar amounts of this salt and 1-chloro-3-bromopropane (5 mmol+5 mmol) were mixed in hexanes at about -25° C., and the mixture was allowed to warm to about 0° C. while swirling over 45 minutes. The mixture was cooled to -25° C. again, and 10 mmol of t-butyllithium in pentane was added. The resulting mixture was allowed to warm slowly to room temperature and agitated gently overnight before use. It was estimated that 0.28M active Li was present and 0.24M, with 0.34M total base, was found. The mixture was used to initiate the polymerization of butadiene and styrene as described in the following examples.

EXAMPLE 2. Polymerizations of styrene/butadiene  
mixtures using hexamethyleneiminopropyllithium

Polymerizations were run using the initiator solution prepared according to Example 1 hereinabove. The following table (TABLE III) lists the ingredients and conditions used in the polymerizations. A 0.24M solution of the above initiator was added to a dried, sealed, nitrogen-purged bottle, through a Viton rubber cap liner, to a 75 percent/25 percent by weight blend of butadiene and styrene in hexanes, at an estimated level of 0.75 milliequivalent ("mequiv.") active C-Li/100 grams monomer, and an additional amount of N,N,N',N'-tetramethylethylenediamine ("TMEDA") was added at the TMEDA/Li ratio indicated in TABLE III.

TABLE III

POLYMERIZATION OF STYRENE/BUTADIENE

	SAMPLE A	SAMPLE B
Amount (g) of Monomer	90.6	95.3
ml of 2.0 M TMEDA (TMEDA/Li)	0.42 (1:1)	0.43 (1:1)
Initiator, mequiv	0.82	0.86
Initiator, ml	2.91	3.06
Pzn temperature, ° C.	80	80
Pzn time, minutes	40	40

The mixtures were agitated at 80° C. for 0.5 to 2.5 hours ("hr"), proceeding to approximately 94-98 percent conver-

sion to polymer. In practice, there is considerable leeway in the reaction times and temperatures, much the same as there is leeway in the reaction vessels, type of agitation, etc., used. The treated cements then were quenched by injection with 1.5 ml of i-PrOH (isopropyl alcohol), treated with an anti-oxidant (3 ml of a mixture containing 1.6 wt % dibutyl paracresol (DBPC) in hexane), coagulated in i-PrOH, air-dried at room temperature, then drum-dried. Suitable characterization tests were performed. Analyses of the product polymer are given in TABLE IV (Run A).

**EXAMPLE 3.** Polymerizations of styrene/butadiene mixtures using hexamethyleneiminopropylolithium and end-linking with  $\text{SnCl}_4$

The procedure of Example 2 was followed, except that after 40 minutes of polymerization at 80° C., the polymerization mixture was treated with 0.8 equiv. of  $\text{SnCl}_4$  per equivalent ("equiv.") of Li charged. The mixture was agitated at 50° C. for 30 minutes. The product was isolated and dried in the same manner as above. It showed about 40 percent coupling in the 80° C. polymerization. Analyses of this polymer are also given in TABLE IV (Run B).

TABLE IV

ANALYSIS OF COMPOUNDED POLYMERS		
RUN:	SAMPLE A	SAMPLE B
Polymer recovered %	94	95
$\tan \delta$ , ° C. (DSC, onset)	-43.9	-44.2
ML/4/100, raw	62.4	96.2
GPC (THF):		
$M_n$	202762	248129
$M_w/M_n$	1.25	1.94

**EXAMPLE 4.** Compounded evaluations of polymers made from hexamethyleneiminopropylolithium

The product polymers (from Runs A and B of Table IV) were compounded and tested as indicated in the test recipe shown in TABLE II, and cured 20 min @ 165° C. Compared to the control polymer, the results of the compounded evaluations are summarized in TABLE V. A control polymer, (a tin-coupled styrene/butadiene rubber ("SBR") initiated with t-butyllithium) was also compounded and tested. Compared to the control polymer, the product of Run A exhibited improved hysteresis loss characteristics and enhanced interaction with carbon black, compared to unmodified elastomers of the same molecular weight embodied in the control polymer. In these experiments, the polymers were of higher molecular weight than anticipated, since the initiator was part of a mixture.

TABLE IV

POLYMER ANALYSIS			
Feature	Polymer Sample i <sup>a</sup>	Polymer Sample A <sup>b</sup>	Polymer Sample B <sup>c</sup>
	Sn-Coupled Control (BuLi <sup>d</sup> initiator)	HMI-Pr-Li <sup>e</sup> 80° C.	HMI-Pr-Li 80° C./SnCl <sub>4</sub>
ML/4-Raw	74	62.4	96.2
ML/4-Cpd	67.3	107.1	116.1
#1 Dispersion Index %	95.0	89.9	76.7

TABLE IV-continued

POLYMER ANALYSIS			
	Polymer Sample i <sup>a</sup>	Polymer Sample A <sup>b</sup>	Polymer Sample B <sup>c</sup>
Dynastat 1 Hz, $\tan \delta$ , 50° C.	0.0934	0.0895	0.0926

<sup>a</sup>Control SBR

<sup>b</sup>Inventive polymer prepared according to Example 2

<sup>c</sup>Inventive polymer prepared according to Example 3

<sup>d</sup>butyllithium

<sup>e</sup>Hexamethyleneimine propylolithium

It is clear from the foregoing examples and specification disclosure, that the present invention provides novel cyclic aminoalkyllithium compounds useful for example, as anionic polymerization initiators for the preparation of diene monomers. Reproducible polymerization of such polymers within a relatively narrow molecular weight range is achieved, and the resulting polymers also exhibit good preservation of live C-Li ends which permits further polymer functionalization through the use of terminating reagents.

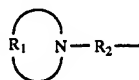
It is to be understood that the invention is not limited to the specific initiator reactants, monomers, terminators, polar coordinators or solvents disclosed herein, except as otherwise stated in the specification. Similarly, the examples have been provided merely to demonstrate practice of the subject invention and do not constitute limitations of the invention. Those skilled in the art may readily select other monomers and process conditions, according to the disclosure made hereinabove.

Thus, it is believed that any of the variables disclosed herein can readily be determined and controlled without departing from the scope of the invention herein disclosed and described. Moreover, the scope of the invention shall include all modifications and variations that fall within the scope of the attached claims.

What is claimed is:

1. A functionalized elastomer comprising:

a functional group defined by the formula

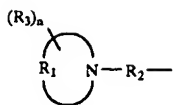


where  $\text{R}_1$  is a selected from the group consisting of a divalent alkylene group, an oxy-alkylene group, an amino alkylene group, and a substituted alkylene group, each group having from about 6 to about 20 carbon atoms,  $\text{R}_2$  is covalently bonded to the elastomer and is selected from the group consisting of a linear-alkylene group, a branched-alkylene group, and a cyclo-alkylene group, each group having from about 2 to about 20 carbon atoms.

2. A functionalized elastomer, as set forth in claim 1, where  $\text{R}_1$  has from about 6 to about 12 carbon atoms.

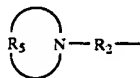
3. A functionalized elastomer, as set forth in claim 1, where  $\text{R}_2$  has from about 3 to about 12 carbon atoms.

4. A functionalized elastomer, as set forth in claim 1, wherein said functional group is defined by the formula



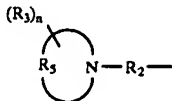
where  $R_1$  is a selected from the group consisting of a divalent alkylene group, an oxy-alkylene group, and an amino alkylene group, each group having from about 6 to about 20 carbon atoms,  $R_2$  is covalently bonded to the elastomer and is selected from the group consisting of a linear-alkylene group, a branched-alkylene group, and a cyclo-alkylene group, each group having from about 2 to about 20 carbon atoms and  $R_3$  is selected from the group consisting of a tertiary amino group having from 1 to about 12 carbon atoms, an alkyl group having from 1 to about 12 carbon atoms, an aryl group having from about 6 to about 20 carbon atoms, an aralkyl group having from about 7 to about 20 carbon atoms, an alkenyl group having from about 2 to about 12 carbon atoms, a cycloalkyl group having from about 5 to about 20 carbon atoms, a cycloalkenyl group having from about 5 to about 20 carbon atoms, a bicycloalkyl group having from about 6 to about 20 carbon atoms, and a bicycloalkenyl group having from about 6 to about 20 carbon atoms, and where  $n$  is an integer of from 1 to about 10.

5. A functionalized elastomer, as set forth in claim 1, wherein said functional group is defined by the formula



where  $R_2$  is covalently bonded to the elastomer and is selected from the group consisting of a linear-alkylene group, a branched-alkylene group, and a cyclo-alkylene group, each group having from about 2 to about 20 carbon atoms, and  $R_5$  is selected from the group consisting of a divalent alkylene, an oxy-alkylene, an amino-alkylene group, and a substituted alkylene, where each group has from about 4 to about 20 carbon atoms; a substituted nitrogen group having the general formula  $R_6N$  where  $R_6$  is selected from the group consisting of an alkyl group having from 1 to about 12 carbon atoms; a cycloalkyl group having from about 5 to about 20 carbon atoms; an aryl group having from about 6 to about 20 carbon atoms; and an aralkyl group having from about 7 to about 20 carbon atoms and mixtures thereof; with the limitation that said functional group has from about 2 to about 4 nitrogen atoms and a total of from about 6 to about 24 atoms in the ring structure thereof.

6. A functionalized elastomer, as set forth in claim 5, wherein said functional group is defined by the formula



where  $R_2$  is covalently bonded to the elastomer and is selected from the group consisting of a linear-alkylene group, a branched-alkylene group, and a cyclo-alkylene group, each group having from about 2 to about 20 carbon atoms,  $R_5$  is selected from the group consisting of a divalent alkylene, oxy-alkylene, and amino-alkylene groups, where

each group has from about 4 to about 20 carbon atoms; a substituted nitrogen group having the general formula  $R_6N$  where  $R_6$  is selected from the group consisting of an alkyl group having from 1 to about 12 carbon atoms; a cycloalkyl group having from about 5 to about 20 carbon atoms; an aryl group having from about 6 to about 20 carbon atoms; and an aralkyl group having from about 7 to about 20 carbon atoms and mixtures thereof; with the limitation that said functional group has from about 2 to about 4 nitrogen atoms and a total of from about 6 to about 24 atoms in the ring structure thereof, and  $R_3$  is selected from the group consisting of a tertiary amino group having from 1 to about 12 carbon atoms, an alkyl group having from 1 to about 12 carbon atoms, an aryl group having from about 6 to about 20 carbon atoms, an aralkyl group having from about 7 to about 20 carbon atoms, an alkenyl group having from about 2 to about 12 carbon atoms, a cycloalkyl group having from about 5 to about 20 carbon atoms, a cycloalkenyl group having from about 5 to about 20 carbon atoms, a bicycloalkyl group having from about 6 to about 20 carbon atoms, and a bicycloalkenyl group having from about 6 to about 20 carbon atoms, and where  $n$  is an integer of from 1 to about 10.

7. A vulcanizable composition comprising:

a plurality of elastomers, where at least one of said elastomers has a functional group defined by the formula

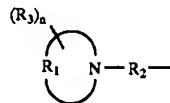


where  $R_1$  is selected from the group consisting of a divalent alkylene group, an oxy-alkylene group, an amino alkylene group, and a substituted alkylene group, each group having from about 6 to about 20 carbon atoms, and  $R_2$  is covalently bonded to the elastomer and is selected from the group consisting of a linear-alkylene group, a branched-alkylene group, and a cyclo-alkylene group, each group having from about 2 to about 20 carbon atoms.

8. A vulcanizable composition of matter, as set forth in claim 7, where  $R_1$  has from about 6 to about 12 carbon atoms.

9. A vulcanizable composition of matter, as set forth in claim 7, where  $R_2$  has from about 3 to about 12 carbon atoms.

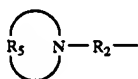
10. A vulcanizable composition of matter, as set forth in claim 7, wherein said functional group is defined by the formula



where  $R_1$  is selected from the group consisting of a divalent alkylene group, an oxy-alkylene group, and an amino alkylene group, each group having from about 6 to about 20 carbon atoms;  $R_2$  is covalently bonded to the elastomer and is selected from the group consisting of a linear-alkylene group, a branched-alkylene group, and a cyclo-alkylene group, each group having from about 2 to about 20 carbon atoms, and  $R_3$  is selected from the group consisting of a tertiary amino group having from 1 to about 12 carbon atoms, an alkyl group having from 1 to about 12 carbon

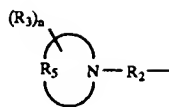
atoms, an aryl group having from about 6 to about 20 carbon atoms, an aralkyl group having from about 7 to about 20 carbon atoms, an alkenyl group having from about 2 to about 12 carbon atoms, a cycloalkyl group having from about 5 to about 20 carbon atoms, a cycloalkenyl group having from about 5 to about 20 carbon atoms, a bicycloalkyl group having from about 6 to about 20 carbon atoms, and a bicycloalkenyl group having from about 6 to about 20 carbon atoms, and where n is an integer of from 1 to about 10.

11. A vulcanizable composition of matter, as set forth in claim 7, wherein said functional group is defined by the formula



where  $\text{R}_2$  is covalently bonded to the elastomer and is selected from the group consisting of a linear-alkylene group, a branched-alkylene group, and a cyclo-alkylene group, each group having from about 2 to about 20 carbon atoms,  $\text{R}_5$  is selected from the group consisting of a divalent alkylene, an oxy-alkylene, an amino-alkylene group, and substituted alkylene, where each group has from about 4 to about 20 carbon atoms; a substituted nitrogen group having the general formula  $\text{R}_6\text{N}$  where  $\text{R}_6$  is selected from the group consisting of an alkyl group having from 1 to about 12 carbon atoms; a cycloalkyl group having from about 5 to about 20 carbon atoms; an aryl group having from about 6 to about 20 carbon atoms; and an aralkyl group having from about 7 to about 20 carbon atoms and mixtures thereof; with the limitation that said functional group has from about 2 to about 4 nitrogen atoms and a total of from about 6 to about 24 atoms in the ring structure thereof.

12. A vulcanizable composition of matter, as set forth in claim 5, wherein said functional group is defined by the formula



where  $\text{R}_2$  is covalently bonded to the elastomer and is selected from the group consisting of a linear-alkylene group, a branched-alkylene group and a cyclo-alkylene group, each group having from about 2 to about 20 carbon atoms, where  $\text{R}_2$  is covalently bonded to the polymer,  $\text{R}_5$  is selected from the group consisting of a divalent alkylene, oxy-alkylene, and amino-alkylene groups, where each group has from about 4 to about 20 carbon atoms; a substituted nitrogen group having the general formula  $\text{R}_6\text{N}$  where  $\text{R}_6$  is selected from the group consisting of an alkyl group having from 1 to about 12 carbon atoms; a cycloalkyl group having from about 5 to about 20 carbon atoms; an aryl group having from about 6 to about 20 carbon atoms; an aralkyl group having from about 7 to about 20 carbon atoms and mixtures thereof; with the limitation that said functional group has from about 2 to about 4 nitrogen atoms and a total of from about 6 to about 24 atoms in the ring structure thereof, and  $\text{R}_3$  is selected from the group consisting of a tertiary amino group having from 1 to about 12 carbon atoms, an alkyl group having from 1 to about 12 carbon atoms, an aryl group having from about 6 to about 20 carbon atoms, an aralkyl group having from about 7 to about 20 carbon atoms, an alkenyl group having from about 2 to about 12 carbon atoms, a cycloalkyl group having from about 5 to about 20 carbon atoms, a cycloalkenyl group having from about 5 to about 20 carbon atoms, a bicycloalkyl group having from about 6 to about 20 carbon atoms, and a bicycloalkenyl group having from about 6 to about 20 carbon atoms, and where n is an integer of from 1 to about 10.

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